CHAPTER I
INTRODUCTION

In last decade, intrinsically conductive polymers including polyaniline, polypyrrole, polyacetylene, polythiophene, polyphenylene vinylene, *etc.* have been extensively synthesized by either chemical or electrochemical method. These conductive polymers have conjugated double bonds as a backbone which can easily be reduced and oxidized due to low ionization potential and high electron affinity. Consequently, their electrical conductivity can be altered ranging from the insulating to semi-conducting regions.

Among the mentioned conductive polymers, polyaniline (PANI) is one of the most attractive conductive polymers because of its facile synthesis, good environmental stability, ease of electrical conductivity control by changing an oxidation state as well as a protonation state, and low cost of monomer. PANI has shown promising commercial viability in technological applications such as rechargeable batteries, conductive coatings or adhesives, electromagnetic shielding, electrical and electrochemical devices, and gas separation membranes. However, the infusibility and insolubility in common solvents of PANI are the major problems that hamper its applications. Many attentions have been given to improve the processability of PANI by fabricating composite materials between PANI and other polymer matrixes. However, poor dispersability of PANI in the matrixes has become severe problem in some properties, especially the mechanical properties, and applications of the obtained composite product. Therefore, the use of PANI nanoparticles instead of their macroscopic counterpart may be another route used to address this problem.

PANI nanoparticles can be synthesized by various approaches broadly classified into template synthesis and no template synthesis. However, it is well known that template synthesis is an effective method to produce the PANI nanoparticles with controllable in size and shape, although, post-synthesis process is usually required in order to remove of templates and, moreover, such treatments run the risk of causing destruction or aggregation of the resulting PANI nanoparticles. Thus, the finding of some materials that can behave like template in the condition for

PANI synthesis and can be easily removed after the polymerization is completed has great challenged.

In this present study, biosurfactants was investigated as a template to synthesize the PANI nanoparticles. The biosurfactants was produced from bacteria *Pseudomonas aeruginosa* SP4 strain, gram–negative bacteria, which excrete a mixture of biosurfactants with a glycolipids structure. These are known as rhamnolipids. The rhamnolipids provide good physicochemical properties in term of surface activities, stabilities, and emulsification activities, consequently, it is active to form micelles and stable dispersion in the reaction medium. Additionally, the micelles of the rhamnolipids can trap some hydrophobic substances suggesting the possibility to serve as the template for monomer accumulation and subsequent polymerization.

The purpose of this work is to synthesize PANI nanoparticles by using an oxidative polymerization of aniline in the presence of the biosurfactants, as the template. The effects of the amount of aniline, the concentration of biosurfactants, the concentration of acid dopant, and the reaction time on morphology, thermal property, and electrical conductivity of the synthesized PANI products was also investigated.

1.1 Theoretical Background

1.1.1 Surfactants

The term surfactant was coined by Antara Products in 1950, which is a blend of word "SURface ACTive AgENT". Surfactant is amphiphathic molecules with both hydrophobic (tail) and hydrophilic (head) moieties. Therefore they are capable of reducing surface and interfacial tension at the interfaces between liquids, solids and gases, thereby allowing them to mix or disperse readily as emulsions in water or other liquids. Many surfactants can also assemble in the bulk solution into aggregates. Examples of such aggregates are vesicles and micelles. The concentration at which surfactants begin to form micelles is known as the critical micelle concentration or CMC. When micelles form in water, their tails form a core that can encapsulate an oil droplet, and their (ionic/polar) heads form an outer shell that maintains favorable contact with water. When surfactants assemble in oil, the

aggregate is referred to as a reverse micelle. In a reverse micelle, the heads are in the core and the tails maintain favorable contact with oil as shown in Figure 1.1.
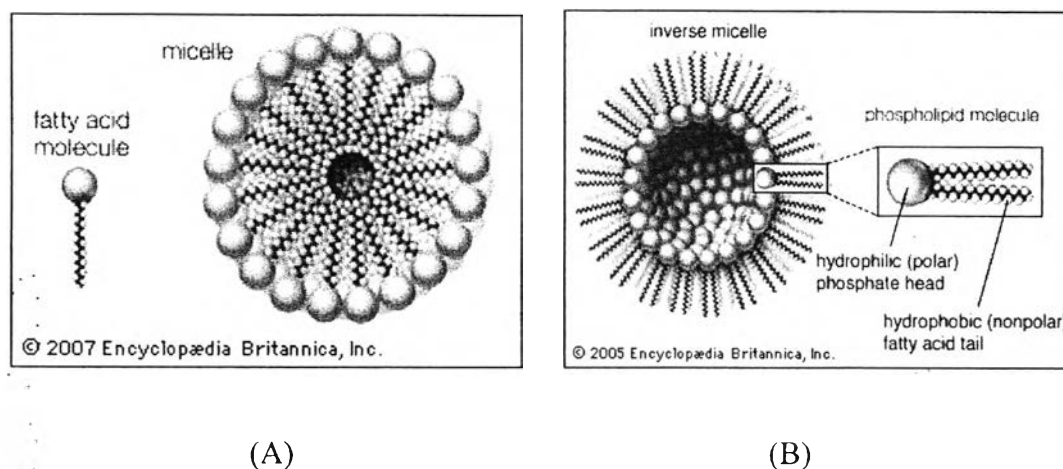

(A)   (B)

Figure 1.1 Schematic of (A) micelle and (B) inverse micelle structure.
(http://media-2.web.britannica.com, 25/03/09, 11.30a.m.).

1.1.1.1 Classification of Surfactants

Surfactants are also often classified into four primary groups; non-ionic, cationic, anionic, and zwitterionic (dual charge). The four basic classes of surfactant are defined as below: (Myers *et al.*, 1992)

1.1.1.1.1 Nonionic Surfactant

The hydrophilic group has no charge, but derives its water solubility from highly polar group such as poloyoxyethylene ($-OCH_2CH_2O-$) or polyol groups. Examples of nonionic surfactants including polysorbate, cocamide MEA, etc.

1.1.1.1.2 Anionic Surfactant

The hydrophilic group carrying a negative charge such as carboxyl ($RCOO^-M^+$), sulfonate ($RSO_3^-M^+$), or sulfate ($ROSO_3^-M^+$). Examples of anionic surfactants, including perfluorooctanoate (PFOA), perfluorooctanesulfonate (PFOS), sodium dodecyl sulfate (SDS), etc.a

1.1.1.1.3 Cationic Surfactant

The hydrophilic group bearing a positive charge such as the quaternary ammonium halides ($R_4N^+Cl^-$). The cationic surfactants including cetyl trimetylammonium bromide (CTAB), cetyl pyridinium chloride (CPC), polyethoxylated tallow amine (POEA), etc.

1.1.1.1.4 Amphoteric (and Zwitterionic)

The hydrophilic group carrying both a negative and positive charge, such as the sulfobetaines $RN^+(CH_3)_2CH_2CH_2SO_3^-$. The zwitterionic surfactants including ocamidopropyl betaine (CAPB), etc.

Moreover, surfactant can be classified into two main groups: synthetic surfactants and biosurfactants.

1.1.2 Biosurfactants

Due to the environmental problem from synthetic surfactant produced by organic chemical reaction, thereby many researcher pay attention on biosurfactants because of they are produced by microorganisms such as bacteria, yeasts, and fungi as shown in table 1, and in particular in bacteria which grow on a substrate which is a source of food for example vegetable oil and crude oil spillage treated with selected microorganisms. The numerous advantages of biosurfactants, such as mild production conditions, lower toxicity, higher biodegradability, lower irritancy, biocampatibity and environmental compatibility. Because of these superior properties, biosurfactants have a potential use in food, pharmaceutical, and cosmetic industries. (Desai and Banat *et al.*, 1997)

Table 1.1 Major types of biosurfactants produce by microorganism (Banat *et al.*, 2000)

Microorganism	Biosurfactant type
Pseudomonas aeruginosa UW-1	Rhamnolipid
Pseudomonas aeruginosa GL-1	Rhamnolipid
Pseudomonas aeruginosa SP4	Rhamnolipid

Pseudomonas aeruginosa J4	Rhamnolipid
Pseudomonas aeruginosa UG2	Rhamnolipid
Pseudomonas aeruginosa AT10	Rhamnolipid
Pseudomonas aeruginosa LBI	Rhamnolipid
Pseudomonas aeruginosa 44T1	Rhamnolipid
Pseudomonas aeruginosa IFO 3924	Rhamnolipid
Pseudomonas aeruginosa ATCC9027	Rhamnolipid
Alcanivorax borkumensis	Glycolipid
Tsukamurella sp.	Glycolipid
Bacillus pumilus A1	Surfactin
Bacillus subtilis PT2	Surfactin
Bacillus subtilis C9	Surfactin
Norcardia SFC-D	Trehalose lipid
Rhodococcus sp. H 13 A	Trehalose lipid

The biosurfactant-producing microbes are distributed among a wide variety of genera. The major types of biosurfactants include: Glycolipids type, Phospholipids type, Lipopeptides and lipoproteins type and Polymeric type. (Desai and Banat *et al.*, 1997)

1.1.2.1   Type of Biosurfactant

Biosurfactant can be divided into four main types based on their biochemical nature and the microbial species. All of these are: (Desai and Banat *et al.*, 1997)

1.1.2.1.1   Glycolipids

They are carbohydrates in combination with long-chain aliphatic acids or hydroxyaliphatic acids. Among the glycolipids, the best known are rhamnolipids, trehalolipids, and sophorolipids.

1.1.2.1.1.1 Rhamnolipids

Rhamnolipid is the one of best-studied glycolipids, produced by several species of *Pseudomonas*. Generally, rhamnolipids contain a hydrophilic head formed by one or two rhamnose molecules and a

hydrophobic tail which is composed of one or two fatty acid chains. The schematic reported by (Pornsunthorntawee *et al.*, 2008) have demonstrated the structure of rhamnolipids as show in Figure 1.2.
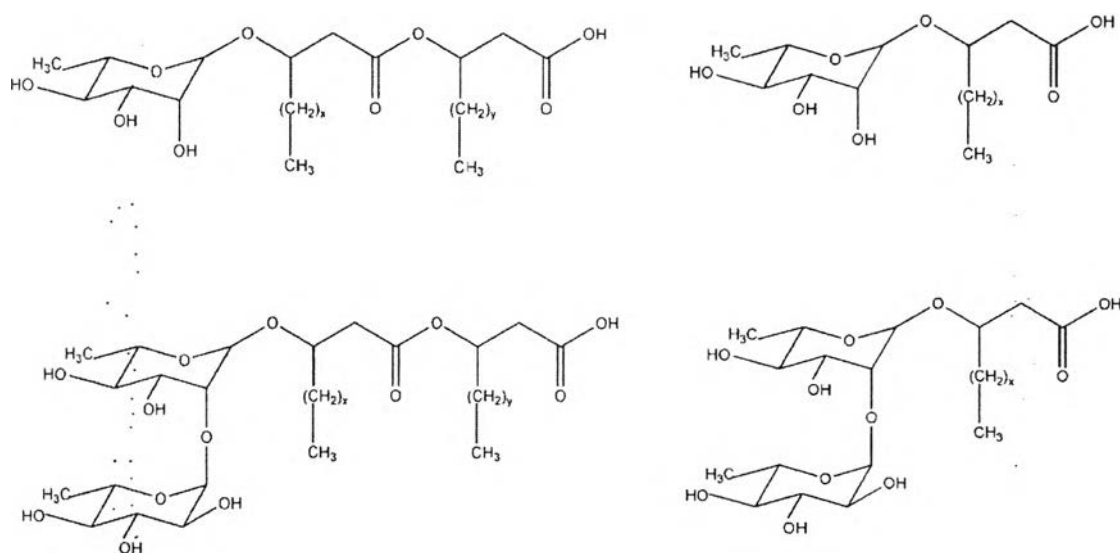

Figure 1.2 Shows the four general chemical structures of rhamnolipids produced by certain species of *Pseudomonas*.

The two major types of rhamnolipids are L-rhamnosyl-3-hydroxydecanoyl-3-hydroxydecanoate, or monorhamnolipid (Rha–C10–C10),andL-rhamnosyl-L-rhamnosyl-3-hydroxydecanoyl-3-hydroxydecanoate, or dirhamnolipid (Rha–Rha–C10–C10). However, most of the biosurfactants produced by *Pseudomonas aeruginosa* strains were reported to be dirhamnolipid, only a few reports showed that monorhamnolipid was the predominant component.

1.1.2.1.1.2 Trehalose Lipids

The structures of trehalose lipids are found several structural types. Their disaccharide trehalose linked at C6 and C6' to mycolic acids is associated with most species of *Mycobacterium, Nocardia, Corynebacterium Arthrobacter* and *Brevibacterium.* Mycolic acids are long-chain, a-branched-bhydroxy fatty acids. Trehalolipids from different organisms differ in the size and structure of mycolic acid, the number of carbon atoms, and the degree of

unsaturation. Desai and Banat *et al.* (1997) showed the structure of trehalose dimycolate produced by *Rhodococcus erythropolis* as shown in Figure 1.3.
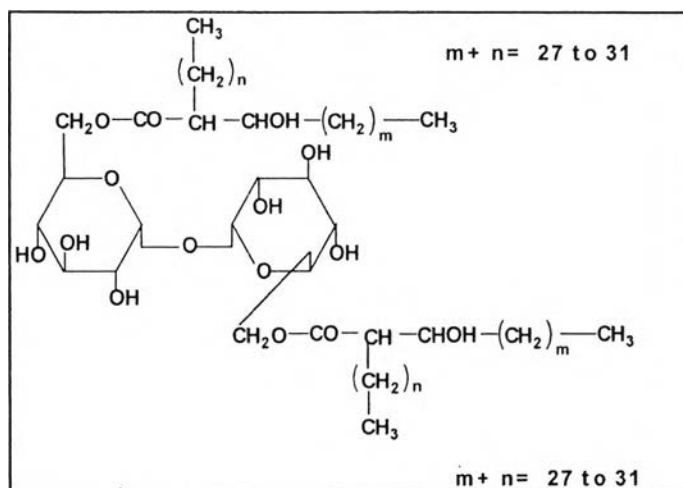

Figure 1.3 Trehalose dimycolate from *Rhodococcus erythropolis*, in which disaccharide trehalose is linked to two long-chains α-branched β-hydroxy fatty acids.

1.1.2.1.1.3 Sophorolipids

Sophorolipid biosurfactants, mainly produced by yeasts such as *Torulopsis bombicola*, *Torulopsis petrophilum*, and *Torulopsis apicola*, consist of a dimeric carbohydrate sophorose linked to a long-chain hydroxy fatty acid as see in Figure 1.4. (Desai and Banat *et al.*, 1997)
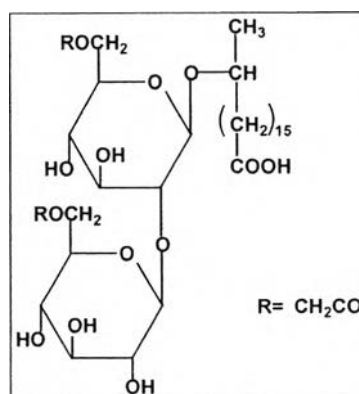

Figure 1.4 Sophorolipid from *Torulopsis bombicola* in which dimeric sophorose is linked to a long-chain (C18) hydroxy fatty acid.

Sophorolipids produced by *T.*
petrophilum which grow on water-insoluble substrates such as alkanes and vegetable oils whereas some sophorolipids, which were chemically identical to those produced by *T. bombicola*, did not emulsify alkanes or vegetable oils. Although sophorolipids can lower surface and interfacial tension, they are not effective emulsifying agents (Desai and Banat, 1997).

1.1.2.1.2 Phospholipids and Fatty Acids

These are the esters formed between the alcohol groups on a lipid and a phosphate. Desai and Banat *et al.* (1997) showed the structure of Phospholipids as in Figure 1.5.
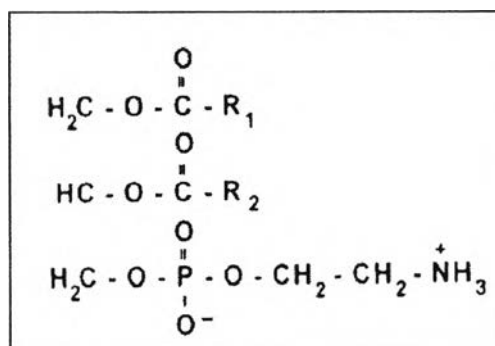

Figure 1.5 Structure of phosphatidylethanolamine produced by *Acinetobacter sp.* R_1 and R_2 are hydrocarbon chains of fatty acids.

1.1.2.1.3 Lipoproteins or Lipopeptides

These consist of a lipid attached to a polypeptide chain. Desai and Banat *et al*, (1997) showed the structure of surfactin as in Figure 1.6.
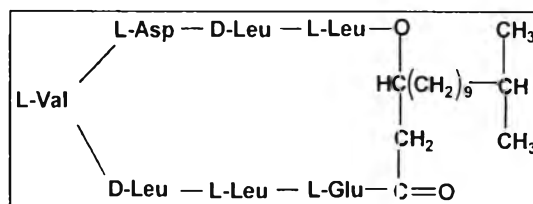
Figure 1.6 Structure of cyclic lipopeptide surfactin produced by *Bacillus subtilis*.

1.1.2.1.4 Polymeric Surfactants

These are products again formed between saccharide units and fatty acid residues; but they are polymeric in nature. These kinds of biosurfactants have high molecular weight biopolymer generally demonstrate useful properties such as, high viscosity, tensile strength, and resistance to shear. Accordingly, polymeric biosurfactants have found a variety of industrial uses. (Healy, Devine and Murphy *et al.*, 1996) The best-studied polymeric biosurfactants are emulsan, liposan, mannoprotein, and other polysaccharide-protein complexes. Desai and Banat *et al.* (1997) showed the structure of emulsan as in Figure 1.7.
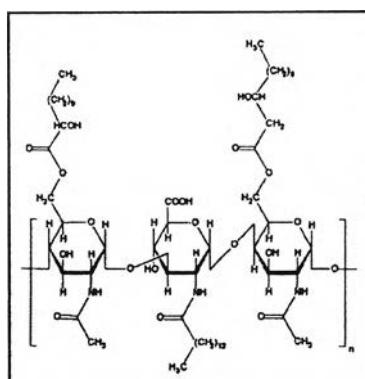

Figure 1.7 Structure of emulsan, produced by Acinetobacter calcoaceticus, in which fatty acids are linked to a heteropolysaccharide backbone.

From the four types listed, it is only the glycolipids group which is of particular interest, since the bacterial species used in this study i.e. *Pseudomonas*

aeruginosa SP4. Pseudomonas strains are able to biosynthesize rhamnose-containing surfactants also known as rhamnolipids as shown in table 1.1.

However, the main limiting factor is the economics of large-scale production of biosurfactants; the main drawbacks being:

(1) Poor yields from raw substrate materials;

(2) Large capital investment;

(3) Reactions are carried out in dilute solution so there is poor volume efficiency for the plant;

(4) Need for sterilisation;

(5) Problems in the control of the process, for example, foaming;

(6) Problems in product recovery and purification;

(7) Difficulties in analysing the finished products chemically due to their complex nature.

1.1.3 Electrically Active Polymers and Composites

Generally, there are four primary types of electrically active polymer system with different degrees of conductivity.

The first and the most widely used conducting polymeric systems are the composites in which an insulating polymer matrix is filled with a particulate or fibrous conductive fillers such as a carbon or a metal to impart high conductivity. Applications for such composites are wide spread, these are used for interconnections, printed circuit boards, encapsulations, die attach, electromagnetic and aerospace engineering.

The second group of polymers is known as ionically conducting polymers. Here, the origin of electrical conductivity is a result of the movement of ions present in the system. An example of such a polymer is polyethylene oxide, in which lithium ions are mobile. These types of polymers have application in the battery industry.

The third group of polymers is known as redox polymers. The system contains immobilized redox centers (electroactive centers). However, these centers are not necessarily in contact with one another, but can conduct charge by electron transfer from one center to another through the well known "hopping" mechanism. During conduction, electrons tunnel from one redox center to another through an

insulating barrier. The systems need to have a large number of redox centers to increase the probability of such tunneling.

The fourth group of conducting system is conjugated polymers. These polymers consist of alternating single and double bonds, creating an extended π-network. The movement of electrons within this π-framework is the source of conductivity. However, dopant is required to increase the level of conductivity for this type of polymers.

1.14 Intrinsically Conducting Polymers (ICPS)

ICPs are inherently conducting in nature due to the presence of a conjugated π electron system in their structure. ICPs have a low energy optical transition, low ionization potential and a high electron affinity. A high level of conductivity (near metallic) can be achieved in ICPs through oxidation–reduction as well as doping with a suitable dopant. The conductivity of a number of ICPs relative to copper and liquid mercury is presented in Figure 1.8.
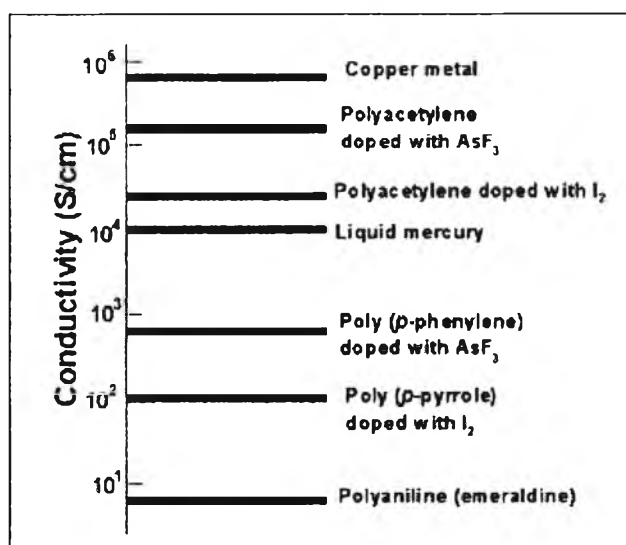

Figure 1.8 The conductivity of a number of ICPs relative to copper and liquid Mercury.

1.1.5 Polyaniline

Polyaniline (PANI) has elicited the most interest since its electric conductivity was found by MacDiarmid et al. [49] in 1985. PANI is an electrically conducting polymer with many features that could be exploited in various applications. Apart from PANI, other conducting polymers, such as polypyrrole, polythiophene, polyacetylene, and poly (p-phenylene-vinylene), etc. have been explored in the past, as shown in Figure 1.9.
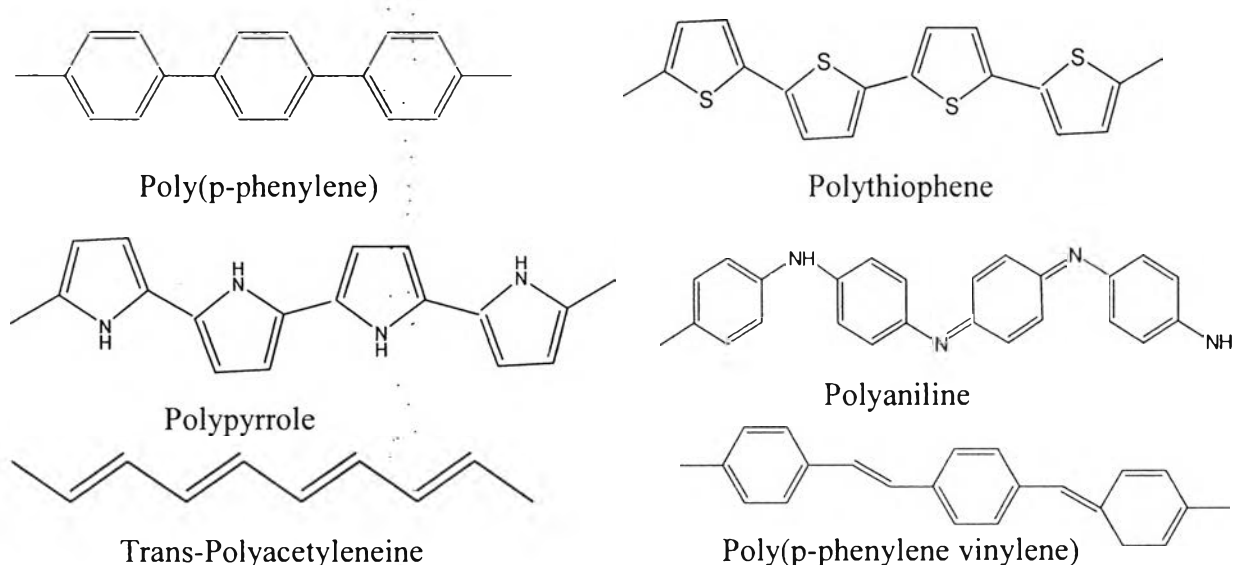
Poly(p-phenylene)

Polythiophene

Polypyrrole

Polyaniline

Trans-Polyacetyleneine

Poly(p-phenylene vinylene)

Figure 1.9 Examples of conducting polymers.

PANI has been most extensively studied because it exhibits good environmental stability, its electrical properties can be modified by changing the oxidation state as well as protonation of PANI chains , its wide range of conductivity from insulating to metallic regime, unique redox enability, low cost, ease of synthesis, and promising applications in various fields, such as metallic corrosion protection, electromagnetic interference shielding, electrostatic discharge , sensors, actuators, to mention just a few.

PANI exists in various oxidation states ranging from fully reduced form, leucoemeraldine (LM), the nitrogen atoms are amines, to fully oxidized form ,pernigraniline (PNA), all the nitrogen atoms are imines. The 50% oxidized material,

emeraldine, contains equal numbers of amine and imine units, each containing two nitrogen atoms. However, among various forms of PANI, only the emeraldine salt is conducting. The leucoemraldine form has a band gap of nearly 4 eV, whereas the emeraldine base and fully oxidized pernigraniline forms have a band gap of the order of 2 eV. [39] PANI exists in three stable oxidation states as shown in Figure 1.10.
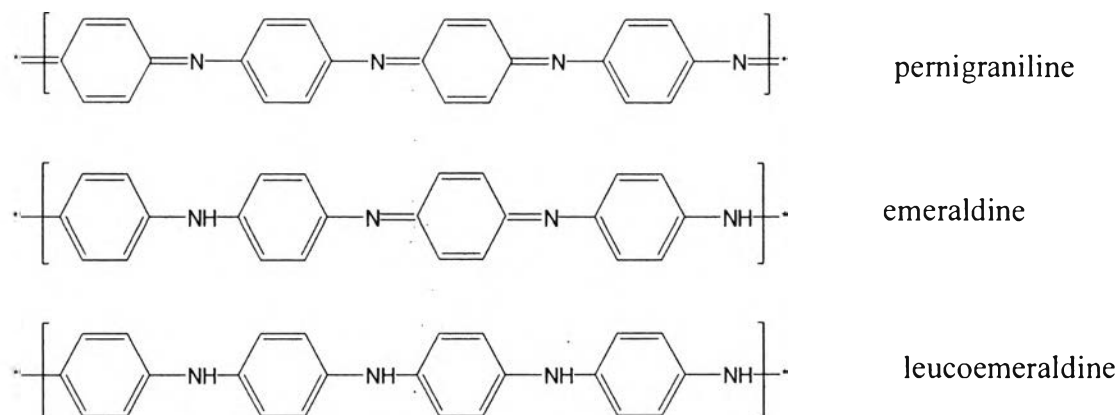

Figure 1.10 The oxidation state of PANI.

It is well established that PANI can be transformed into a conducting state, the emeraldine salt form (PANI ES), via a doping process with acids such as HCl, and can be converted to an insulating state, the emeraldine base form (PANI EB), by treatment with bases such as NH_4OH or $NaOH$, referred to as the dedoping process as shown in Figure 1.11.

However, the intractability, i.e., infusibility and insolubility, is the main factor that hampers the applications of PANI, dispersing of the PANI in conventional polymers was considered one of the most effective approaches to address this problem. Accordingly, synthesis of nano-structured PANI, on one hand, is the key step in preparing highly dispersed blend of PANI with other processable polymers, and thus to improve the processability of PANI. On the other hand, some special physical and chemical properties differing from the bulk material will be achieved on nano-structured PANI and will render it for new applications , such as chemical sensors, energy conversion and storage, light-emitting display devices, microelectronics, optical storage, and so on.
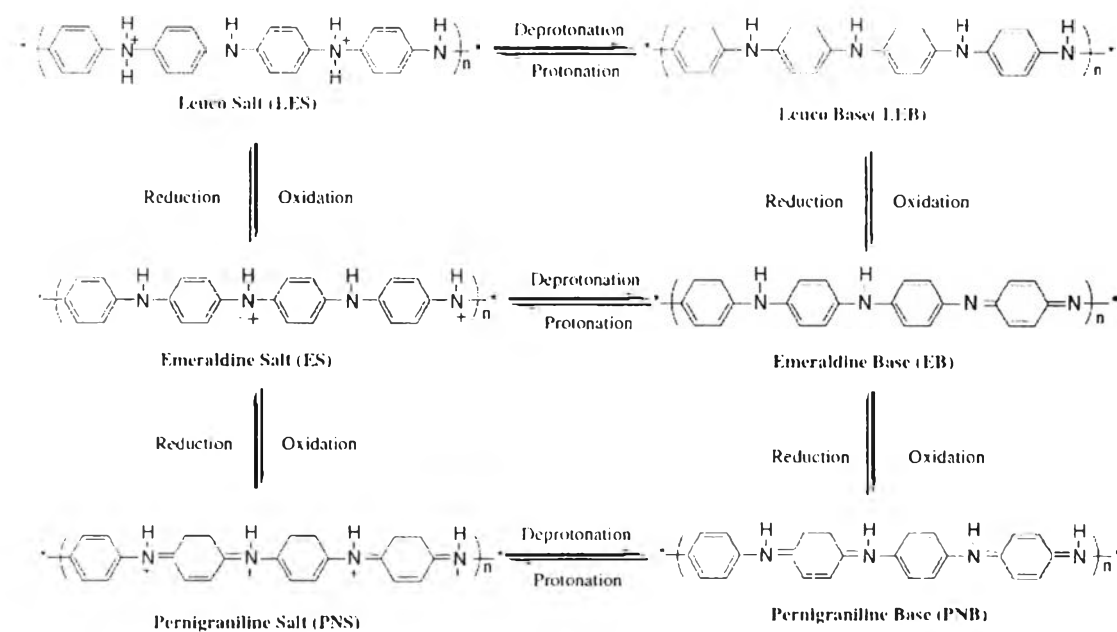
Figure 1.11 Molecular structure of PANI in emeraldine base and emeraldine salt form.

One dimensional nano-structured PANI, including nanofibers, nanowires, nanorods, nanotubes, nanofibrils, nanobelts and nanoribbons, presents several advantages in fabricating nano-devices and in preparing nanoscale electrical connections in highly conducting polymer composites, etc. Moreover, the processability of PANI can be readily improved by increasing its solubility in organic solvents. Doping of PANI with protonic acids such as camphorsulfonic acid (CSA) or dodecylbenzenesulfonic acid (DBSA) is known to increases the solubility of emeraldine salt form in solvents such as *m*-cresol, xylene, etc. This is because of the negatively charged sulfonate group of the dopant that associates with the positively charged backbone of the emeraldine salt form of the polymer through Coulomb attraction thereby providing a hydrophobic side chain compatible with organic solvents. DBSA is known for its surfactant action but can act simultaneously as a dopant. Another approach to improve processability of this material has been to prepare them as colloidal nanoparticles. Different strategies have been employed for the preparation of PANI dispersions in colloidal form.

1.1.6 Synthesizing Approaches

PANI and its derivatives are generally synthesized by chemical or electrochemical oxidative polymerization of the monomers, although some other approaches such as plasma polymerization, electroless polymerization and solid-state polymerization were also reported. In addition; the synthesizing approaches used for production of one-dimensional nano-structured PANI are divided into two categories, i.e. the template synthesis and the no-template synthesis. The former is subdivided into hard template (physical template) synthesis and soft template (chemical template) synthesis approach according to the solubility of the templates in the reacting media, while the latter is subdivided into interfacial polymerization, radiolytic synthesis, rapid mixing reaction method and sonochemical synthesis. Other approaches like seeding polymerization and combined soft and hard template synthesis were also reported. However, the potential synthesizing approaches that efficiency to control the morphology and sizes of synthesized nanoparticles were the hard template and soft template synthesis method.

1.1.6.1 Hard Template

The hard template synthesis method, involves synthesizing the intrinsically conducting polymers like PANI, polypyrrole, as well as other materials including metals, carbons, in the pores, channels of hard templates such as membranes, zeolites, anodic aluminum oxide (AAO), and so on. One of the interesting and useful features of the method is its effectiveness in preparing one-dimensional micro- or nano-structured materials with controllable diameter, length and orientation. However, the disadvantage of the method is that, firstly, a rather tedious post-synthesis process is required in order to remove the templates ; secondly, the nano-structured polymers may be destroyed or form undesirable aggregated structures after released from the templates

1.1.6.2 Soft Template

The soft template synthesis method, always called the template-free method or self-assembly method in the literatures in that no hard templates is used, entails synthesizing the PANI, as well as polypyrrole, in the presence of structure-directing molecules such as surfactants, deoxyribonucleic acid (DNA), polyelectrolytes, thiolated cyclodextrins, sulfonated porphyrin, liquid

crystalline, and ethanol, which act as templates for production of the one-dimensional nanomaterials. This method is simple and cheap in comparison with the hard template method because it omits the use of the hard templates and therefore the wearisome post synthesis processing.

1.1.6.3 Interfacial Polymerization

When polymerization reaction is carried out in the interfaces of two immiscible solvents it is known as interfacial polymerization. PANI has been synthesized by an interfacial polymerization technique using a mixture of two immiscible solvents such as water and chloroform in the presence of different acids acting as dopants. The reaction is initiated by an oxidizing agent such as APS, H_2O_2, and so on at room temperature or at any preferable temperature in the presence or absence of a surfactant. The final product is isolated
by centrifugation.(Progress in preparation)

1.1.6.4 Seeding Polymerization

The seeding polymerization is a typical template approach where a foreign material is used as the seed and the polymerization reaction is carried out in the presence of this seed. PANI nanofiber has been synthesized from aniline in the presence of some PANI powder acting as a "seed" using different acid dopants and different solvents. The PANI obtained by this method is similar to a nanofiber with high conductivity. The morphology of this nanofiber depends upon the type of acid used, the acid concentration, type of seed, the solvent used, and the relative amount of seed with respect to solvent. Among these reaction conditions, the influence of monomer concentration and solvent type was found to be pronounced in the morphology of the resultant PANI. .(Progress in preparation)

1.1.6.5 Sonochemical Synthesis

The sonochemical process is initiated with the dropwise addition of an acidic APS solution to an acidic aniline solution, similar to that of conventional PANI synthesis. However, the polymerization is accomplished with the aid of ultrasonic irradiation. While
during the sonochemical synthesis, the further growth and agglomeration of the primary nanofibers are effectively prevented (even if more aniline and APS were added into the system), following the formation of more primary PANI nanofibers.

One of the advantages of this approachis its scalability in comparison with other approaches such as interfacial polymerization or rapid mixing reaction. .(Progress in preparation)

1.1.6.6 Electrochemical Synthesis

At present there is a twofold interest in the electrochemical polymerization (ECP) process. Firstly, the ECP reaction provides a better method of polymerization with a fine control of the initiation and termination steps. Secondly, ECP has a degree of technological potential. The electrochemical reactions are often much cleaner, and the PANI obtained is expected to be in a relatively purer form (as no additional chemicals such as surfactant,

oxidant, and so on are used here) compared to that obtained from chemical polymerization. Furthermore, the use of limited chemicals reduces the problem of pollution. Electrochemical methods are generally employed for the polymerization of aniline under: (i) a constant current (galvanostatic); (ii) a constant potential (potentiostatic); and (iii) a potential scanning/cycling or sweeping. The first method essentially consists of a two-electrode assembly dipped in an electrolyte solution containing the monomer, and a specified level of current is passed to form PANI film on the surface of a platinum foil electrode. The polymerization of aniline at a constant potential produces polymer powder which adheres weakly on the electrode.